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Catalytic Oxidation of Phosphines by Transition Metal-Activated Carbon Dioxide

by

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The complexes $(Ph_3P)_3RhCl$ and $(cyclooctene)_2RhCl_2$ have been found to catalyze the oxidation of phosphines by carbon dioxide in refluxing decalin. The rate of oxidation increases in the order $PPh_3 < PBuPh_2 < PEt_3$.

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CATALYTIC OXIDATION OF PHOSPHINES BY TRANSITION METAL-ACTIVATED CARBON DIOXIDE

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Summary

The complexes $(Ph_3P)_3RhCl$ and $[(cyclooctene)_2RhCl]_2$ have been found to catalyze the oxidation of phosphines by carbon dioxide in refluxing decalin. The rate of oxidation increases in the order $PPh_3 < PBuPh_2 < PEt_3$.

As the world's petroleum reserves dwindle, there is an intensive search underway for alternative fuels and organic feedstocks. This has stimulated considerable interest in the potential activation of carbon dioxide by means of transition metal complexes[1]. Although a few discreet CO_2 complexes have been reported[2-7], in several cases, reactions of carbon dioxide with metal complexes have yielded carbonyl and carbonate or oxide species - products of CO_2 disproportionation[7-11]. In a few instances, e.g. in reactions of CO_2 with $(C_2H_4)Mo(diphos)_2$[12] and $(R_3P)_3RhCl$[13], stoichiometric O-atom transfer to phsophine apparently occurs, producing phosphine oxide, either free or coordinated. We now report that under appropriate conditions, phosphines can be oxidized by carbon dioxide <u>catalytically</u> in the presence of $[(cyclooctene)_2RhCl]_2$ or $(Ph_3P)_3RhCl$ (eq. 1).

$$CO_2 + PR_3 \xrightarrow[\text{decalin}]{L_3Rh(I)X} OPR_3 + CO \qquad \text{(eq. 1)}$$

When a decalin solution of triphenylphosphine containing one mole % of $(Ph_3P)RhCl$ or $[(C_8H_{14})_2RhCl]_2$ is refluxed (ca. 185°C) under an atmosphere of purified CO_2*, triphenylphosphine oxide is slowly produced (turnover number ca. 20/day) as indicated by the growth of IR bands at 1210, 1115, and 720cm^{-1}**. After several days, high yields of Ph_3PO (m.p. 148-151°, lit[16] 150-152) could be obtained upon cooling the mixture. The co-production of CO was confirmed by the gradual formation of a MnO_2/Ag precipitate when

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*"Bone dry" grade CO_2 was passed first through a Cr(II)/$HClO_4$ solution, then through a dry ice trap, and finally over 3A molecular sieves.

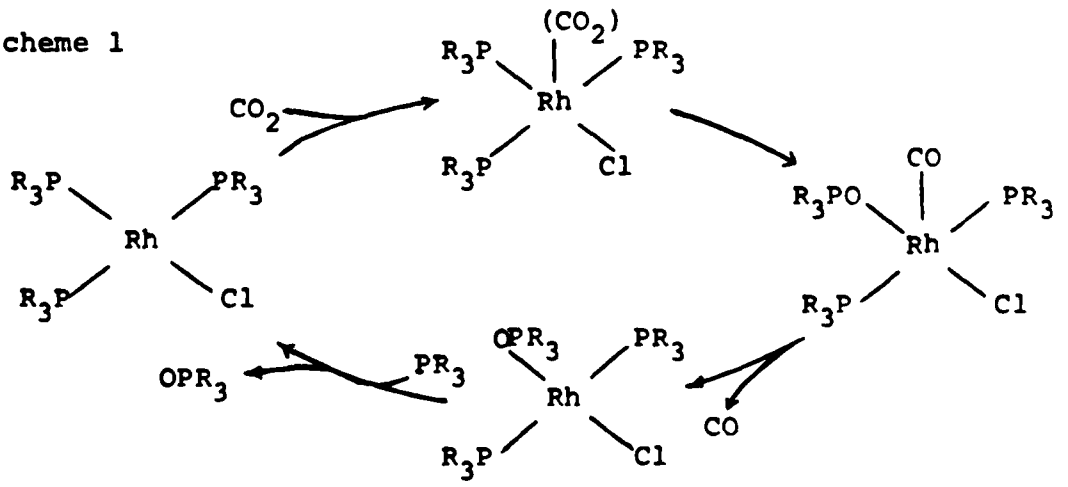
**No reaction was observed in the absence of $(PPh_3)_3RhCl$ or under a nitrogen atmosphere.

the exit gases were passed through an aqueous $KMnO_4/AgNO_3$ solution[17].

Other phosphines are also oxidized under these conditions and qualitatively, the rate of reaction parallels the phosphine basicity. Thus, while the oxidation of PPh_3 was complete only after 7-8 days, $PBuPh_2$ was totally converted to $OPBuPh_2$ after 3 days, and PEt_3 to OEt_3 in less than 44 hrs.

We do not as yet have any direct mechanistic information on these reactions and so any proposed mechanisms at present are best considered somewhat speculative. However, in view of the reported conversion of $(R_3P)_2Rh(CO_2)Cl$ to $(R_3P)(R_3PO)Rh(CO)Cl$[13] and our observation of the lesser catalytic activity of $(PPh_3)_2Rh(CO)Cl$ compared to $(PPh_3)_3RhCl$ (precluding the intermediacy of the former), we suggest the following scheme as a reasonable working hypothesis.

Scheme 1



Kinetic studies are in progress as are efforts to establish the scope of transition metal-mediated CO_2 oxidations with other catalysts and substrates.

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References

1. For a recent review see: M.E. Volpin and L.S. Kolominikov, Organometallic Reactions, vol. 5, 313 (1975);

2. M. Aresta, C.F. Nobile, V.G. Albano, E. Forni, M. Manassero, Chem. Comm., 636 (1975).

3. M. Aresta and C.F. Nobile, J. Chem. Soc. Dalton, 708 (1977).

4. I.S. Kolminikov, A.I. Gusev, G.G. Alexandrov, T.S. Lobeeva, Y.T. Struckov, and M.E. Volpin, J. Organometal. Chem., 59, 349 (1973).

5. B.R. Flynn and L. Vaska, J. Am. Chem. Soc., 95, 508 (1973).

6. G. Fachinetti, C. Floriani, and P. Zanazzi, ibid, 100, 7403 (1978).

7. T. Herskovitz, J. Am. Chem. Soc., 99, 2391 (1977).

8. J. Chatt, M. Kubota, G. Leigh, F.C. March, R. Mason, and D.J. Yarrow, Chem. Comm., 1033 (1974).

9. S. Krogsrud, S. Komiya, T. Ito, J.A. Ibers, and A. Yamamoto, Inorg. Chem., 15, 2798 (1976).

10. G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, J. Am. Chem. Soc., 101, 1767 (1979).

11. G.O. Evans, W.F. Walter, D.R. Mills, and C.A. Streit, J. Organometal. Chem., 144, C34 (1978).

12. T. Ito and A. Yamamoto, J. Chem. Soc. Dalton, 1398 (1975).

13. M. Aresta and L.F. Nobile, Inorg. Chim. Acta., 24, L 49 (1977).

14. G.M. Kosolapoff, J. Am. Chem. Soc., 64, 2982 (1942).

15. "The Chemists' Companion," A.J. Gordon and R.A. Ford, Wiley and Sons, N.Y., p. 440 (1972).